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**CONSTITUTION OF ORDERING ALLOYS
OF THE SYSTEMS Cu-Au AND Co-Pt**

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JULY 1953

WRIGHT AIR DEVELOPMENT CENTER

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Metals Research Laboratory*

July 1953

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RDO No. 461-1-20*

**Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio**

FOREWORD

This report was prepared by the Metals Research Laboratory of the Carnegie Institute of Technology, Pittsburgh, Pennsylvania, under USAF Contract AF 33 (616)-39. It covers all work done on this project and summarizes all significant results obtained during the period from July 1951 to July 1953. The work is a continuation of fundamental studies in the field of order-disorder transformations in alloys, which had been initiated with a fund placed with the Carnegie Institute of Technology by the Moraine Products Division of the General Motors Corporation. The work was administered under the direction of the Aeronautical Research Laboratory, Directorate of Research, Wright Air Development Center, with Captain Ronald E. Sellers, Jr. acting as project engineer. It is identified under RDO No. 461-1-20, "A Study of Order-Disorder in the Cobalt-Platinum System".

ABSTRACT

That portion of the copper-gold phase diagram pertaining to ordering alloys, in the composition range 19.5 to 70 atomic percentage gold, has been determined with greater precision and more completely than previously. Everywhere, except at the stoichiometric compositions of Cu_3Au and CuAu , the regions of order and of disorder are separated by two-phase fields, bounded on the high and low temperature sides respectively by conjugate disorder and order curves. The order curves have been located accurately for the first time. A eutectoid equilibrium, corresponding to the decomposition of the disordered phase simultaneously into the ordered Cu_3Au and CuAu phases, occurs near 36 atomic percentage gold and 284°C . Beneath the eutectoid, and separating the fields of Cu_3Au and CuAu , is a two-phase field of $\text{Cu}_3\text{Au} + \text{CuAu}$, extending from about 35 to 40 atomic percentage gold. There is no intermediate phase near 41 atomic percentage gold, such as had been proposed by Haughton and Payne. Near 70 atomic percentage gold there is a reversal of the electrical resistance change accompanying ordering, that may be associated with the ordered CuAu_3 phase, recently discovered by Ogawa and Watanabe. The alloy of 66 atomic percentage gold has a very low electrical coefficient of resistivity, which becomes almost zero in the temperature range from 240° to 270°C . An incomplete study of the ordering alloys of the system Co-Pt indicates the existence of conjugate order and disorder boundaries, as in the copper-gold system.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



LESLIE B. WILLIAMS
Colonel, USAF
Chief, Aeronautical Research Laboratory
Directorate of Research

TABLE OF CONTENTS

	Page
I. Introduction	1
II. Materials	4
III. Experimental Equipment	6
IV. Experimental Procedure	8
V. Results of Equilibrium Studies on Copper-Gold Alloys .	9
VI. Rates of Approach to Equilibrium in Copper-Gold Alloys	17
VII. Studies Upon the System Cobalt-Platinum	30
VIII. Discussion	33
IX. Conclusions	34
X. Bibliography	35

LIST OF TABLES

	Page
I. Composition of Copper-Gold Alloys	5
II. Composition of Cobalt-Platinum Alloys	5
III. Equilibrium Datum Points for the System Copper-Gold	14

LIST OF FIGURES

	Page
1. Haughton and Payne's Phase Diagram of the System Copper-Gold	2
2. Schematic Drawing of the Specimen Assembly	7
3. Typical Resistivity-Temperature Curves	10
4. Derivation of Disordus and Ordus Curves from a Resistivity-Temperature Plot	12
5. Partial Phase Diagram of the System Copper-Gold	15
6. Some Typical Debye-Scherrer Patterns of Alloys 25, 37 and 49 Stabilized at 270°C	16
7. Schematic Representation of a Typical Time-Resistivity Plot, Temperature Constant	19
8. Time-Resistivity Plot for Alloy 25, Progressing from Equilibrium at 410°C to Equilibrium at 395°C	20
9. Time-Resistivity Plot for Alloy 36, Progressing from Equilibrium at 338 1/4°C to Equilibrium at 292 3/4°C	22
10. Time-Resistivity Plot for Alloy 32, Progressing from Equilibrium at 298 3/4°C to Equilibrium at 293 3/4°C	23
11. Time-Resistivity Plot for Alloy 50, Progressing from Equilibrium at 413°C to Equilibrium at 411°C	24
12. Time-Resistivity Plot for Alloy 50, Progressing from Equilibrium at 410 3/4°C to Equilibrium at 413 1/2°C	25
13. Time-Resistivity Plot for Alloy 47, Progressing from Single-Phase Equilibrium at 410 1/2°C to Two-Phase Equilibrium at 407°C	26
14. Time-Resistance Plots for Alloy 43, Progressing from Equilibria respectively at 378 3/4, 375 3/4 and 363 1/4°C to Equilibria at 359 1/2, 365 and 359 1/2°C	28
15. Time Resistivity Plots for Alloys 49 and 50, Progressing from Equilibrium at 414 3/4°C to Equilibrium at 411°C	29
16. Resistivity-Temperature Curve for Co-Pt (46 atomic percentage) measured at temperature	31
17. Resistivity-Temperature Curve for Co-Pt (46 atomic percentage) measured after quenching to Room Temperature	32

CONSTITUTION OF ORDERING ALLOYS OF THE SYSTEMS Cu-Au and Co-Pt

I INTRODUCTION

The copper-gold alloy system is the prototype of a group of systems which are isomorphous at high temperature and which undergo ordering transformations at lower temperature. It is generally accepted that two types of ordered structures are formed, one ideally having equal numbers of atoms of the two metals and being referred to as the CuAu type, the other ideally having three copper atoms for every gold atom and being called the Cu₃Au type. The former is characteristically of tetragonal crystal symmetry, the latter face centered cubic; both transform into an isomorphous face-centered cubic disordered solid solution at higher temperature. There is general agreement also that ordering is not confined to the alloys of ideally stoichiometric composition, but occurs in the copper-gold system in the range from about 18 atomic percentage gold to approximately 70 atomic percentage, or higher.

There have been a number of constitutional investigations of the copper-gold system, of which the most commonly accepted is that of Haughton and Payne¹, Figure 1. These authors presented a phase diagram drawn in accordance with the Phase Rule. The two ordered phases were represented as undergoing congruent transformation at temperature maxima at their respective stoichiometric compositions, existing at lower temperatures as two ordered solid solution series together spanning the composition range of ordering. The conjugate single phase regions were separated, according to rule, by two-phase regions which were estimated to be very narrow. A unique feature of the Haughton and Payne diagram was the representation of a third, possibly ordered, phase near 41 atomic percentage gold, and thought to exist over a very limited temperature range. These conclusions were based largely upon carefully conducted thermal studies. More recent electron diffraction studies by Ogawa and Watanabe², indicate the possible occurrence of yet another ordered phase, CuAu₃, with an ordering temperature of 243°C.

Subsequently, the Haughton and Payne diagram was thrown into doubt as a consequence of the promulgation of a concept of ordering transformation which was incompatible with the existence of Phase Rule type equilibria. This concept contemplated a homogeneous transformation from the disordered to the ordered state, and vice versa, so that no two-phase regions of order plus disorder should exist. Since the evidence of the co-existence of order and disorder at equilibrium was all either indirect, or considered inconclusive, it was thought that the ordered state should not be represented as a unique phase on the phase diagram.

The existence of an intermediate ordered phase was doubted, also, upon the basis that no simple and reasonable pattern of ordered atom arrangement, having the required atomic ratio, could be devised. Furthermore, there was no crystallographic evidence of the existence of such a phase, only thermal evidence.

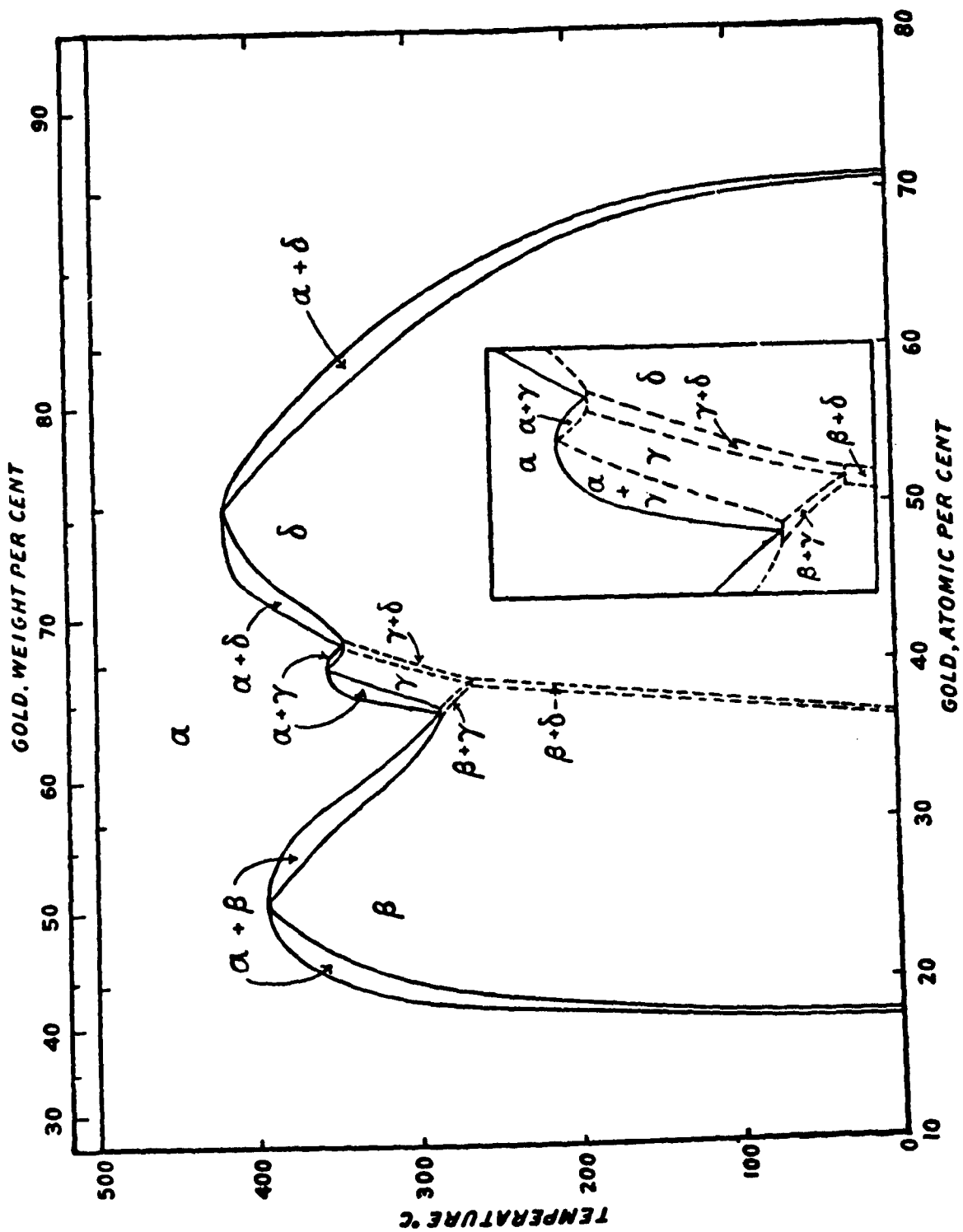


FIGURE 1

The initial portion of the present research dealt with the question of the co-existence, at equilibrium, of the ordered and disordered phases and the results have been published.³ Direct crystallographic evidence of the co-existence of the ordered and disordered phases, at equilibrium, was presented. It was concluded therefrom that the Haughton and Payne diagram is correct in its representation of two-phase equilibria and that the order-disorder transformation is subject to the restrictions of the Phase Rule. These studies were, however, limited to a rather narrow composition range adjacent to the stoichiometric alloy Cu_3Au . In this range it was found that equilibrium is established very slowly at constant temperature and that much of the confusion relative to the nature of the transformation may be assigned to the failure of many of the investigators to achieve equilibrium in their experiments.

There remains a broad range of intermediate alloys whose constitution is imperfectly established and whose transformation characteristics remain almost unstudied. Within this range lies the disputed "intermediate ordering phase". Further knowledge of these alloys is desirable, both to extend the understanding of the ordering characteristics of non-stoichiometric alloys, and, because of a growing technical interest in the heat treatment of analogous alloys, some of which involve useful magnetic properties, in particular the system cobalt-platinum.

Accordingly, the present studies consisted in a re-examination of the constitution of twenty-four ordering alloys covering the range 19.5 to 70 atomic percentage gold, using a technique that was selected for the opportunity that it offered to establish true equilibrium. This consisted in measuring the electrical resistance at a sequence of constant temperatures after sufficient time at each temperature had elapsed to ensure the attainment of equilibrium and proving equilibrium by repeating the process, approaching the equilibrium from the opposite direction. This method is arduous, inasmuch as very long times at constant temperature are required, but it seemed that the questions at issue could scarcely be answered as certainly by less laborious means. The alloy series studied did not include the composition of CuAu_2 (75 atomic percentage gold) because information concerning ordering at this composition appeared too late.

In the process of establishing equilibrium, certain features of the dynamics of the ordering transformations were revealed. From these observations it is apparent that the ordering process proceeds by the nucleation and growth of the precipitating phase, as in all other types of phase transformations. Details of the analyses leading to this conclusion are presented in this report.

II MATERIALS

High purity copper-gold and cobalt-platinum alloys were used in this research; compositions are given in Tables I and II. Charges totalling 10 grams of the purest available grades of electrolytic gold and oxygen-free electrolytic copper were sealed in aqua-dag lined silica glass capsules. At the time of sealing, the capsules were evacuated and partially filled with an atmosphere of purified argon. The assembly was then held in a gas-oxygen flame until the metals were melted, shaken to effect stirring and alternately re-melted and shaken several times to ensure complete mixing. Frozen in the capsule, the resulting ingots were approximately one inch long by $3/16$ inch in diameter. These were annealed 30 hours at 500°C , in argon, to minimize dendritic segregation, and were then cold forged, with intermediate flame annealing, to produce strips that could be further reduced with wire dies. After each heating the surface was removed by filing, to eliminate any oxidized copper and to point the rod for passage through the next die. The final draws, to a finished diameter of 0.017 inch, were made with tungsten carbide dies, in order to ensure roundness and smooth surface. The resulting wires, after a final anneal, became the subject materials of the research.

Cobalt-platinum wires were made for us, at the General Electric Company Laboratories, by melting under nitrogen in magnesia crucibles and then hot swaging the slug to rod and drawing the rod to wire, with annealing treatments, conducted in hydrogen. Details of this procedure have been described by Newkirk, Geisler, Martin and Smoluchowski.⁴

TABLE I
COPPER-GOLD ALLOYS

Nominal Composition		Analyses		
Atomic % Au	Atomic % Au	Weight % Au	Weight % Cu	Total Wt. %
19.5	19.569	43.00	56.96	99.96
22	22.066	46.73	53.24	99.97
25	25.004	50.81	49.16	99.97
28	28.038	54.69	45.28	99.97
32	32.011	59.33	40.65	99.98
35	34.977	62.49	37.45	99.94
36	36.096	63.64	36.32	99.96
37	37.027	64.56	35.40	99.96
38	38.013	65.51	34.44	99.95
39	39.098	66.52	33.40	99.92
40	39.969	67.35	32.61	99.96
41	40.941	68.24	31.73	99.97
42	42.076	69.23	30.72	99.95
43	43.057	70.08	29.88	99.96
45	44.983	71.70	28.27	99.97
47	46.942	73.27	26.70	99.97
49	49.012	74.85	25.11	99.96
50	49.986	75.58	24.39	99.97
51	51.056	76.38	23.59	99.97
54	53.948	78.40	21.58	99.98
59	59.028	81.69	18.28	99.97
64	64.002	84.63	15.35	99.98
66	66.018	85.74	14.23	99.97
70	69.971	87.81	12.15	99.96

TABLE II
COBALT-PLATINUM ALLOYS

Nominal Composition

Atomic % Pt

46
50
70
78
85
90
95

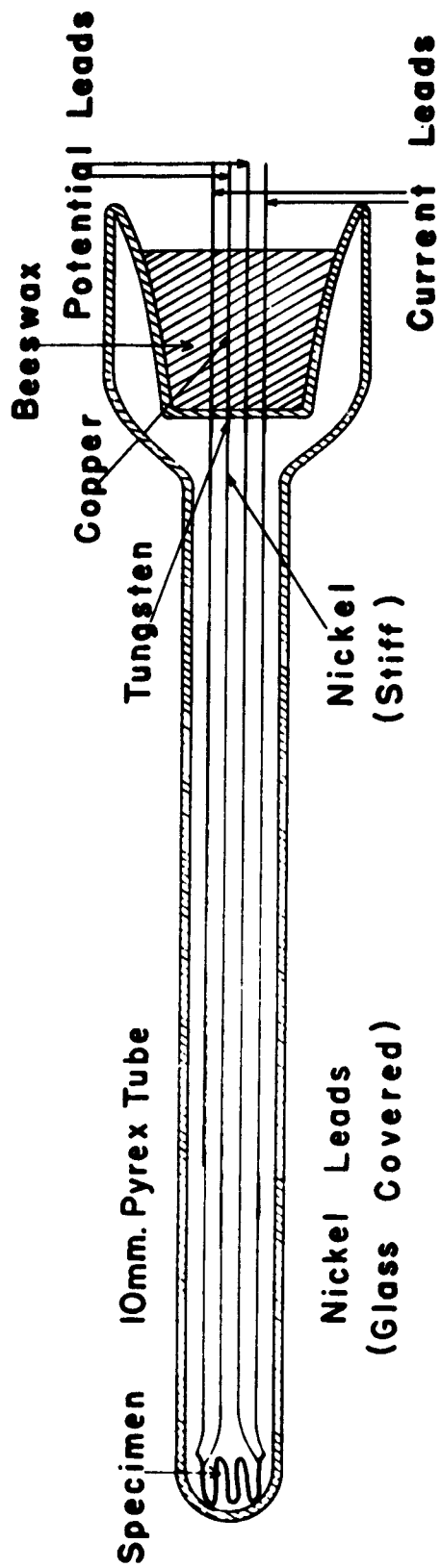
III EXPERIMENTAL EQUIPMENT

Inasmuch as the objective of the research was to establish equilibrium at relatively low temperatures, where a long time at constant temperature would be required, the chief characteristics required of the equipment were: (1) to maintain uniform temperature over the specimen length and constant over long time intervals and (2) to prevent the contamination of the electrical resistance sample by any materials coming in contact with it. The latter requirement was met satisfactorily by maintaining about the wire a stagnant atmosphere of purified argon and by permitting the specimen wire otherwise to come into contact only with tungsten leads and pure alumina insulating beads, all of which materials are of negligible solubility in the alloys concerned, at least at the temperatures of the experiments.

A schematic drawing of the specimen assembly is given in Figure 2. The sample, which was a wire 0.017 inch in diameter and 20 centimeters between potential contact points, was bent into a grid about one inch long, so as to minimize the problem of maintaining a uniform temperature throughout its length. Two current and two potential leads of nickel, with short tungsten wire links, were spot welded to the ends of the specimen and extended about one foot to the cold end of the assembly, where they were spot welded to tungsten glass-seal wires leading to the exterior. The long nickel wires were used in order to avoid heat losses by conduction along the lead wires. Pyrex glass tubing was used for enclosing the copper-gold assemblies, silica glass tubes for the cobalt-platinum alloys. In the latter case, the silica glass tube was joined by a graded seal to a pyrex glass header, through which the lead wires were sealed. There is no evidence that the samples deteriorated chemically, during more than two years at the temperatures of the experiments.

Uniformity of temperature throughout the specimen was maintained without difficulty and constancy of temperature, within $\pm 1/2^{\circ}\text{C}$, was achieved for considerable intervals. But occasional temperature changes of one to three degrees, resulting from causes beyond control, imposed a limitation upon the length of the effective stabilizing periods.

Precautions that were used and that were effective in reducing cycling temperature variations included: (1) the use of six specially designed muffle furnaces having unusually thick temperature lagging upon all sides and ends of the furnace chambers, (2) the use of heavy copper blocks, as thermal reservoirs between the furnace winding and the sample, (3) a voltage stabilizer on the control circuit, (4) a control thermocouple embedded in each furnace winding, (5) thermal insulation about the batteries used in the control circuit, (6) grounded shielding about all thermocouple leads, (7) a rapidly acting Tagliabue six-point temperature controller, (8) the adjustment of the furnace input so as to minimize the lengths of the "on and off" cycles, and (9) the use of boiling distilled water as a temperature reference (cold junction). By these means the temperature cycles were held to something less than $\pm 1/4^{\circ}\text{C}$, with a long interval drift of $\pm 1/2^{\circ}\text{C}$.



SPECIMEN ASSEMBLY

FIGURE 2

Control failures, resulting from power interruptions during electrical storms and from construction work in progress on the campus, plus occasional equipment failures, despite frequent inspection and maintenance, accounted for three or four serious temperature deviations each year. In addition some deviations of from one to three degrees, due to such occurrences as changes in thermocouple characteristics, the line voltage exceeding the control range of the power stabilizer and a miscellany of other causes, further decreased the average interval of really constant temperature to somewhere between one and two months. Ultimately, this problem was dealt with fairly satisfactorily in the analysis of the data, but it had the effect of making nearly impossible the establishment of true equilibrium in those alloys involving the slowest reaction rates.

For temperature measurement, a separate thermocouple placed within the thermal reservoir block, alongside the specimen, was used. Readings made against the temperature of boiling water under known pressure, gave a precision of 0.01°C .

The resistivity of each sample was measured with a Leeds and Northrup Type K potentiometer. In so doing a very small current was used, in order to avoid altering the temperature of the specimen. Prior to taking readings, the current was allowed to flow until all potential drift had ceased. Then the resistivity was measured with the current flowing alternately in opposite directions, and the average of such readings was taken, in order to compensate for stray potentials that might result from temperature differences at various points in the external circuit. This experimental arrangement and procedure made it possible to report the results in terms of true resistance.

All other equipment employed was conventional.

IV EXPERIMENTAL PROCEDURE

The general plan of the experimental procedure was to measure the electrical resistance, at equilibrium, at a series of temperatures covering the range within which the solid state transformations occur, locating the temperatures of these transformations by the occurrence of inflections in the resulting resistance temperature curves. To do this, the sample was held at constant temperature until all resistance change had ceased; then the temperature was lowered, (or raised) by a few degrees and the process repeated, continuing thus until the entire range of interest had been scanned.

By scanning with progressively falling temperature and then with progressively rising temperature, the coincidence of the temperature of the inflections, or lack of coincidence, served to prove, or disprove, the attainment of true equilibrium.

When it was possible to maintain the temperature constant until effective equilibrium had been attained, this state was signaled by constancy in the resistance readings over an extended period. No less than three days of constant resistance was considered adequate, and, where transformation temperatures were being approached closely, this time was extended to a matter of weeks, because it was found that a long induction period usually precedes the beginning of transformation, where the increments of temperature change are small. Prior to the equilibrium studies, a series of non-equilibrium traces were run, in order to locate the approximate temperatures of transformation.

When it was not possible to maintain the temperature constant until equilibrium had been attained, as was the case wherever much more than a month was needed, another procedure was employed. This consisted in utilizing the accidental temperature deviations to indicate how closely equilibrium had been approached. For example, if just prior to an upward temperature deviation the resistance had been falling gradually and continued to decline, despite a temperature rise of a degree or two, then the equilibrium value had not yet been approached at the prior temperature. But if the resistance rises more with a slight temperature increase, than can be accounted for by the thermal coefficient alone, then it is apparent that equilibrium had very nearly been attained. These criteria are most useful where phase changes accompanied by large resistivity changes are occurring within a narrow temperature range; fortunately, this condition prevailed over most of the composition range under study, but there were some areas in which it could not be applied.

As a supplement to the resistivity studies, changes in the crystal structure of the alloys were followed by X-ray diffraction means, using a Debye-Scherrer rotating wire camera. Short pieces of the wires were sealed with argon in small glass capsules and were brought to equilibrium in the same furnaces with the corresponding resistance samples. The resulting photograms were used to identify the phases present, but no attempt was made to determine the relative quantities of the phases, or to measure their lattice spacings. By this means, an estimate of the span of existence of the one and two-phase fields, at sub-critical temperatures was obtained.

V RESULTS OF EQUILIBRIUM STUDIES ON COPPER-GOLD ALLOYS

A maximum of two sharp inflections was found in each of the resistance temperature graphs developed in this study; only in some of those alloys which commenced transformation from the disordered to the ordered state at relatively low temperature was a second inflection at yet lower temperature lacking. The four curves reproduced in Figure 3 illustrate the range of shapes assumed. "Curve "a" represents an isothermal, or nearly isothermal, phase change; curves of this type were encountered only at and adjacent to 25 and 50 atomic percentage gold.

TYPICAL RESISTANCE - TEMPERATURE CURVES

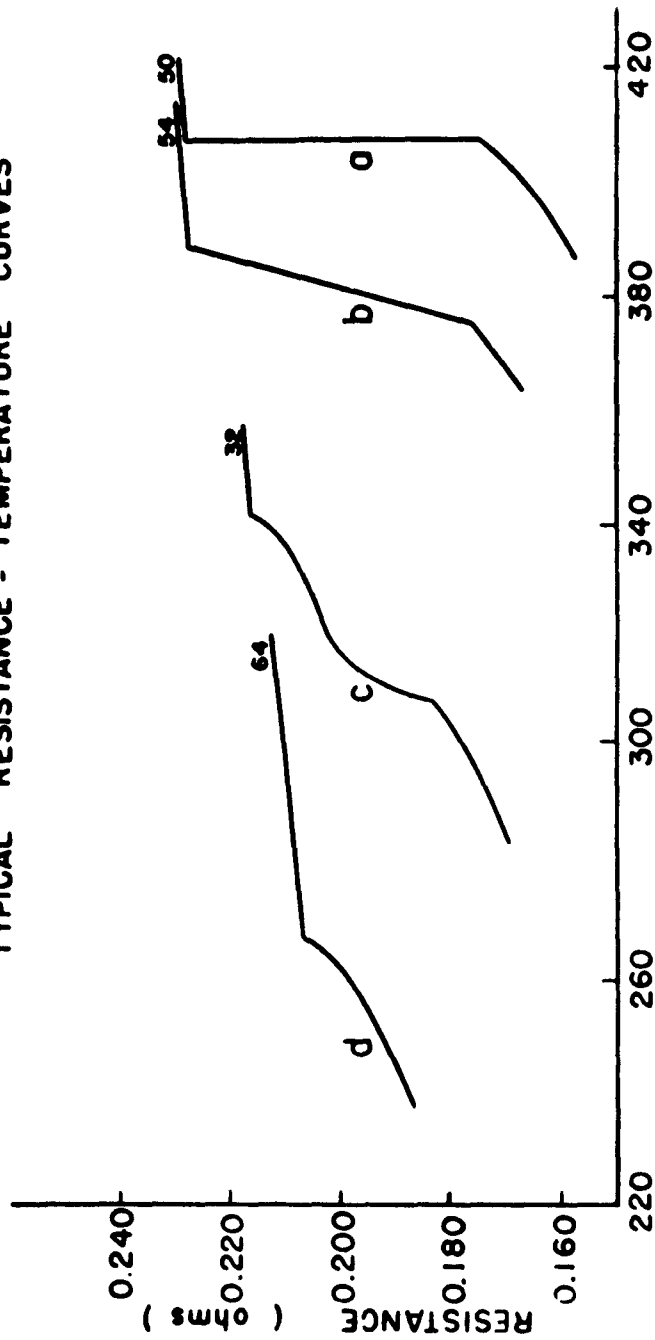
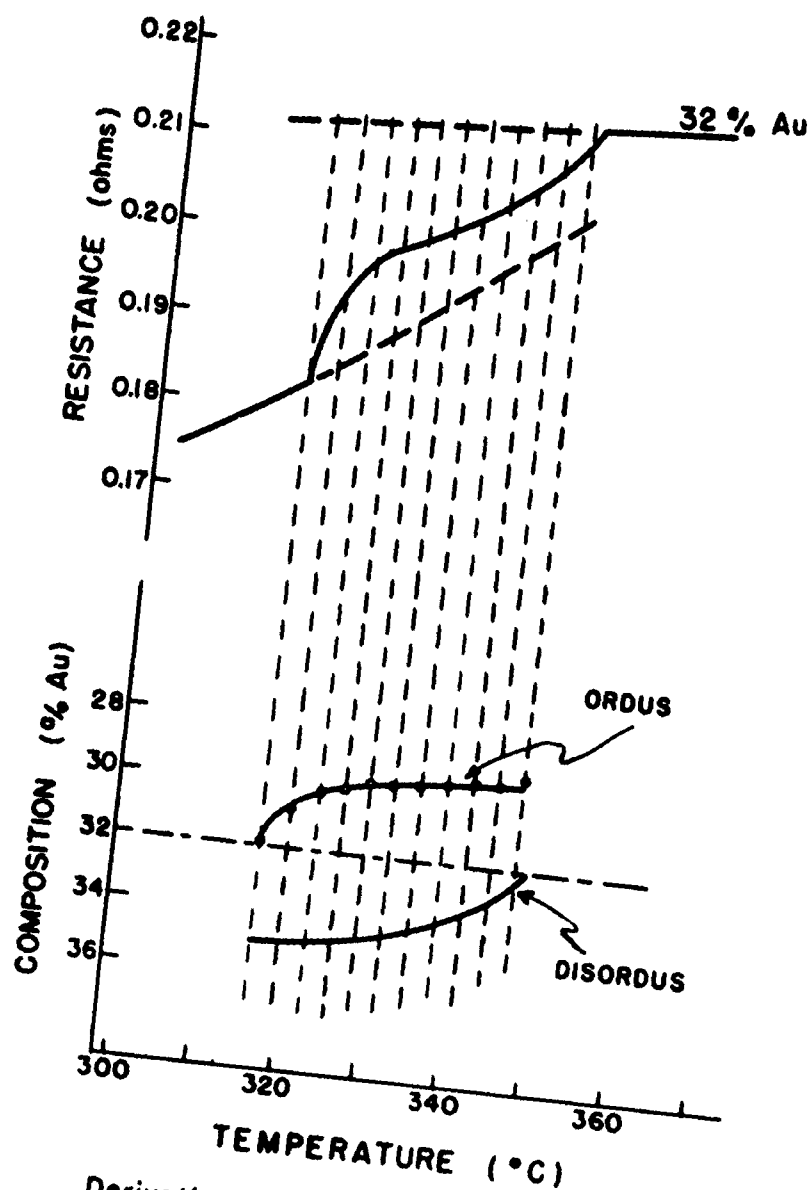


FIGURE 3

Non-isothermal total transformation from a high to a low temperature solid state is indicated by curves of the types "b" and "c" in Figure 3. The first of these corresponds to the condition in which the conjugate solid state boundaries are substantially straight over the temperature range concerned. Such curves were encountered in alloys upon both sides of compositions at which the type "a" curves were found.

The other variation upon non-isothermal transformation, represented by curve "c", can be accounted for upon the basis of substantial curvature of one or both of the conjugate solubility limits, within the temperature range of transformation, and in a manner such that the composition range of two-phase coexistence decreases with declining temperature. The argument is presented in Figure 4. Here it is assumed that the resistance, at a specific temperature within the transformation range, may be computed as a volume average of the extrapolated resistances of the high and low temperature states. Thus, the relative lengths of the two limbs of the tie-line, upon the two sides of the gross composition of the alloy, may be computed, although the absolute length of the tie-line remains unknown. If the further assumption is made that the disorder line (upper transformation limit in the phase diagram) is a smooth curve, it is seen that the order line (lower transformation limit) must curve toward higher gold content at lower temperature. Cases of this kind are found in the composition range between about 30 and 45 atomic percentage gold, except for a narrow range around 36 atomic percentage.

The fourth kind of resistance-temperature curve, type "d", Figure 3, may correspond either to incomplete transformation (no lower inflection) or to an alloy that is stable in a two-phase state at low temperature. From 66 atomic percentage gold upward the curves are the inverse of type "b"; the inflections are in the opposite directions. This means that the low temperature (ordered) phase has higher resistivity than the high temperature (disordered) phase at the same temperature. A type "d" curve, was found at 64 atomic percentage gold. Also at 35 and 36 atomic percentage gold rather similar curves, probably representing failure to attain equilibrium below the upper inflection, were obtained.



Derivation of ordus and disordus curves
from a resistance-temperature plot.

FIGURE 4

A summary of the equilibrium data, obtained from all of the copper-gold alloys, is given in Table III. An estimate of the range of error in the determination of the temperature of each inflection is derived from the uncertainty in locating the inflection upon the resistance-temperature curve. Since all other experimental errors are believed to have been of much smaller magnitude, it is assumed that these may be ignored. The last column of Table III indicates the type of the resistance-temperature curve. From these data have been plotted the ordus and disordus curves of the phase diagram of Figure 5. The temperatures of first inflection correspond to points upon the disordus curve, those of second inflection to points upon the ordus. The shape of the ordus, relative to the disordus, is further checked by the type of the resistance-temperature curve, according to the principle illustrated in Figure 4.

The resistance data fail to define completely the equilibrium relationships in the neighborhood of 36 atomic percentage gold and X-ray diffraction studies were used in an effort to clarify these relationships. In Figure 6 are presented reproductions of three Debye-Scherrer patterns representing the crystal structures of alloys containing 25, 37 and 49 atomic percentage gold, which, after disordering at 500°C, were held at 270°C for 14 days and quenched in water. Shaded areas in these photograms are portions covered with nickel foil, to filter out β radiation. The first of these patterns may be identified as typical of Cu₃Au, the third as typical of CuAu and the second displays both patterns superimposed. Thus, the co-existence of the two ordered phases, Cu₃Au and CuAu, below the minimum in the disordus on the phase diagram of Figure 5 is indicated. In order to obtain an estimate of the span of this two-phase field, all alloys between 28 and 45 atomic percentage gold were similarly examined. The dashed boundaries shown on the phase diagram are rather crude estimates of the immiscibility limits, made by this procedure; at 270°C the two-phase field appears to extend from slightly above 35 to just short of 41 atomic percentage gold.

TABLE III
EQUILIBRIUM DATA FOR THE SYSTEM COPPER-GOLD

SAMPLE NO. (Atomic % gold content)	TEMPERATURE °C		Type of Curve (See Figure 3)
	First Inflection	Second Inflection	
19.5	287 \pm 3	281 \pm 3	b
22	367 \pm 1	352 \pm 2	b
25	390 \pm 1	390 \pm 1	a
28	385 \pm 2	378 \pm 2	b
32	344 \pm 1	312 \pm 2	c
35	302 \pm 3	None Identified	d
36	285 \pm 1	None Identified	d
37	298 \pm 2	290 \pm 3	c
38	321 \pm 3	None Identified	d
39	317 \pm 3	295 \pm 3	b
40	359 \pm 2	339 \pm 1	c
41	365 \pm 1	352 \pm 3	c
42	374 \pm 2	366 \pm 2	c
43	386 \pm 2	371 \pm 2	c
45	403 \pm 3	397 \pm 2	b
47	409 \pm 1	405 \pm 1	a
49	411 \pm 1	410 \pm 1	a
50	411 \pm 1	411 \pm 1	a
51	409 \pm 1	407 \pm 1	a
54	392 \pm 1	379 \pm 2	b
59	344 \pm 2	339 \pm 2	b
64	268 \pm 2	None Identified	d
66	240 \pm 2 (Inverse)	227 \pm 2 (Inverse)	b-Inverse
70	231 \pm 2 (Inverse)	212 \pm 2 (Inverse)	b-Inverse

PARTIAL PHASE DIAGRAM OF THE SYSTEM Cu-Au DERIVED FROM PRESENT RESEARCH

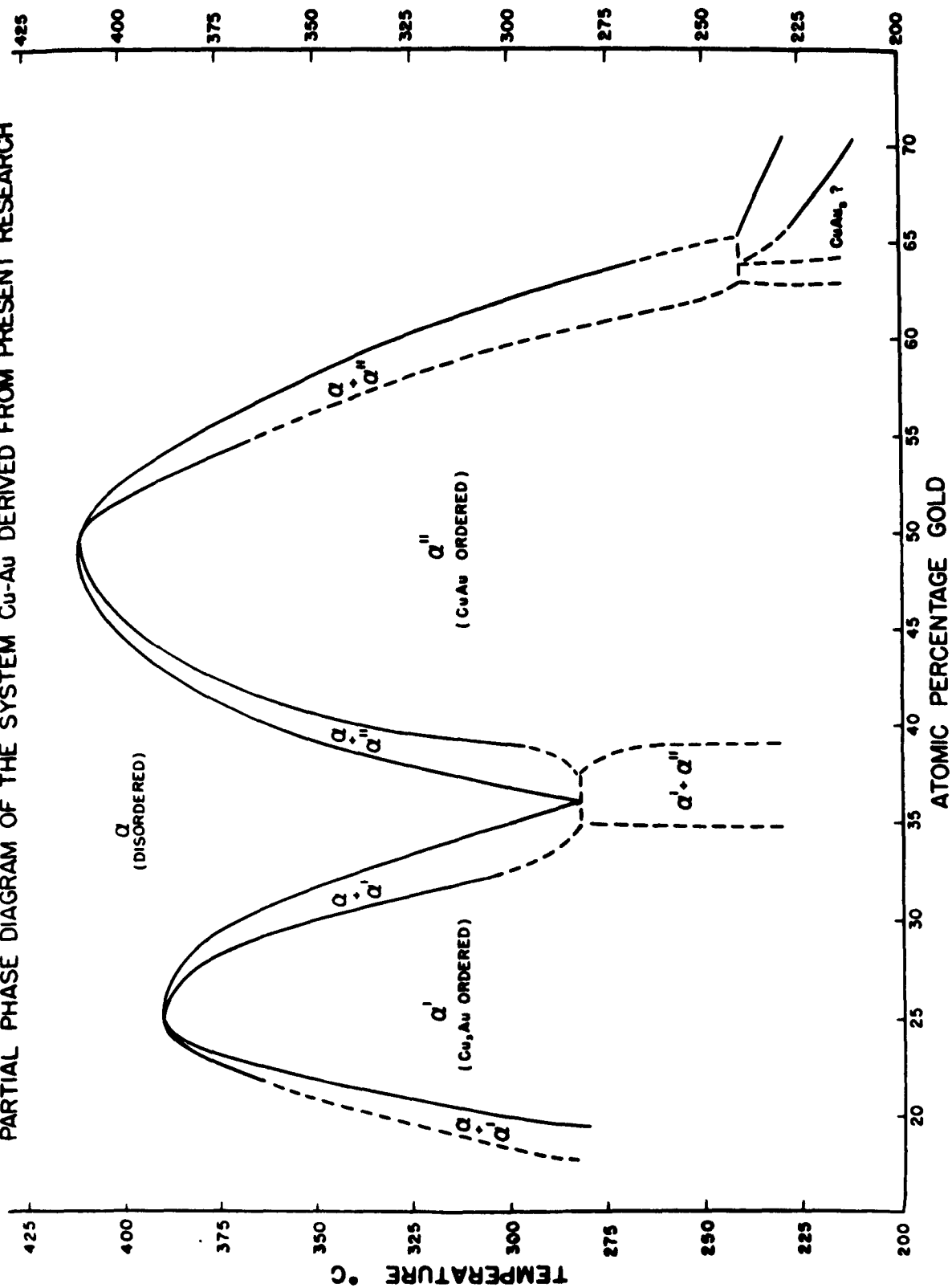
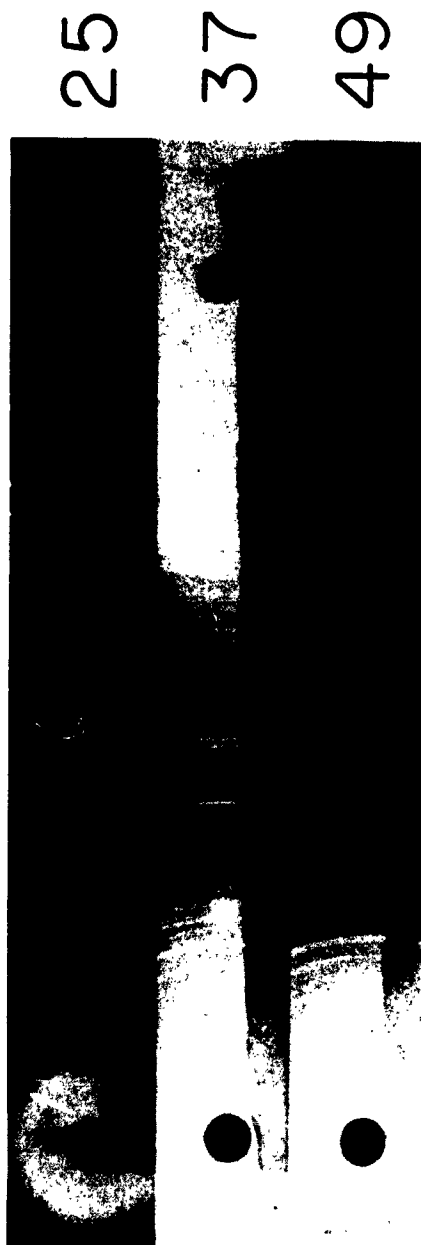


FIGURE 5



Debye - Scherrer patterns of alloys 25, 37, and 49 showing the different patterns of ordered Cu_3Au (25), ordered Cu_3Au plus ordered CuAu (37), and ordered CuAu (49).

FIGURE 6

Constitutionally there are just two possible forms that the phase diagram might assume in the neighborhood of the minimum in the disordus. This point might correspond to a minimum transformation temperature where ordus meets disordus in an isomorphous series between Cu_3Au and CuAu (which is difficult to conceive!), or the minimum might correspond to a eutectoid reaction. That two-phase equilibrium occurs at 270°C in this composition range is strong evidence that eutectoid equilibrium does, in fact, exist. It is surprising, however, that the resistivity-temperature curves failed to register isothermal transformation in this composition range. Two possible explanations present themselves; either the eutectoid reaction is so sluggish that equilibrium was not attained in this range, or the length of the eutectoid reaction tie-line is negligible. It is difficult to decide which of these, if either, is the correct explanation; possibly both contribute to the observed results.

Something new and unexpected is found at 66 and 70 atomic percentage gold. Here the disordus curve assumes a sharply different shape and the presence of an ordus curve is again evident. This has never before been reported. It is at least possible that these configurations are to be associated with the appearance of the newly discovered ordered phase CuAu_3 . Since the data are insufficiently detailed to reveal the constitutional relationships at this inflection in the disordus, it is postulated that a peritectoid equilibrium exists, perhaps among the phases CuAu , CuAu_3 , and the disordered phase, Figure 5. The type "d" curve displayed by alloy 64 is compatible with this proposal, although the occurrence of an isothermal arrest near 230°C would have strengthened the argument.

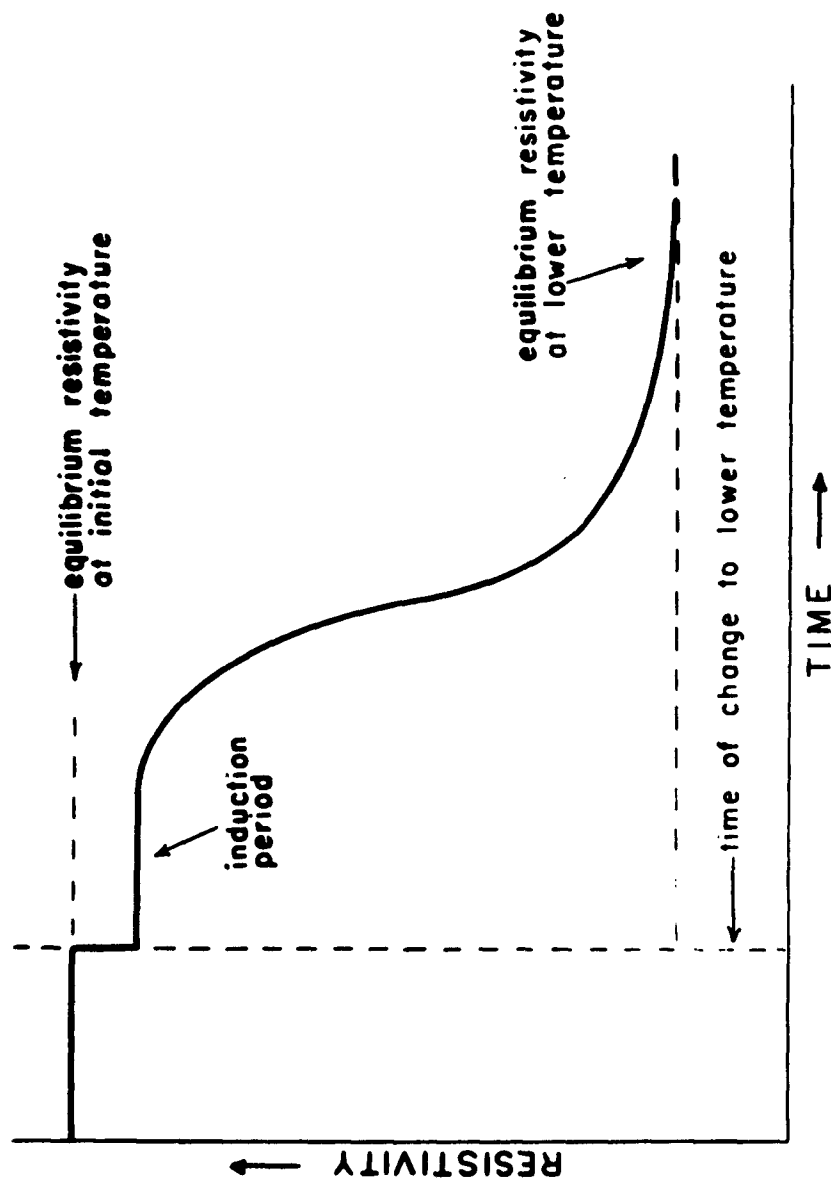
Another noteworthy characteristic of alloy 66 is the almost complete absence of resistance change in the temperature range 240° to 270°C and very little change all the way up to 350°C . Alloys with zero temperature coefficient of resistivity, in this temperature range, are rare; there may be some practical advantage in this characteristic.

VI RATES OF APPROACH TO EQUILIBRIUM IN THE COPPER-GOLD ALLOYS

In following the resistance change in each sample during the periods of establishment of equilibrium, measurements of time-resistance relationships were obtained, which are capable of giving information of value in understanding the mechanism and dynamics of the crystallographic changes that were taking place. These data are so voluminous, however, that it is impractical to do more here than display the several modes of approach to equilibrium that were found and to enumerate some of the conclusions that emerged from a detailed examination of the data.

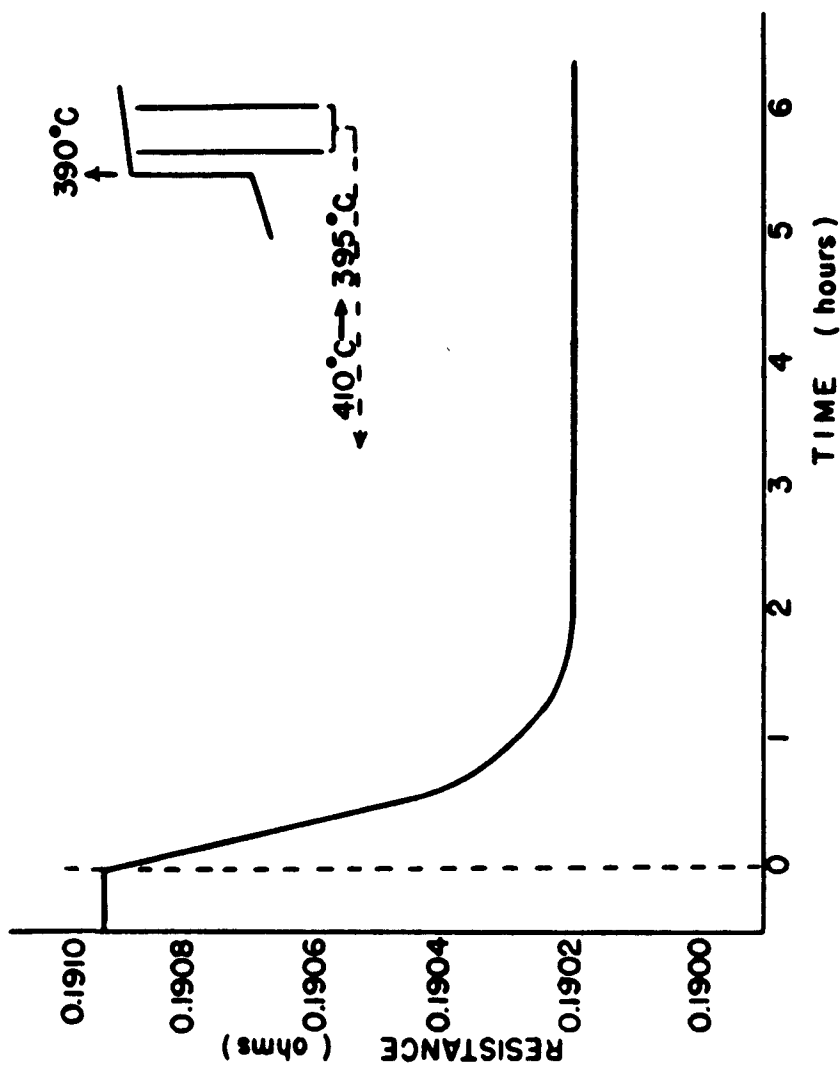
When observed in detail, by taking frequent readings, all time-resistance sequences displayed the essential features of the schematic curve shown in Figure 7. Immediately upon lowering the temperature, from a level at which equilibrium had been established, to a new constant temperature, a few degrees lower, the resistivity decreased by a small amount corresponding to the thermal coefficient of resistivity of the material. Then followed an induction period during which no change in resistance was detected. Presently the resistance began to decrease again at an accelerating pace with a maximum rate of decrease shortly being attained. The rate of decrease then declined gradually to near zero, as the new equilibrium state was approached. In the various alloys and in various temperature ranges this typical curve was modified by the exaggeration or suppression of its several parts.

Steep time-resistance curves, such as that of Figure 8, having almost no induction period, were found to be typical of the approach to equilibrium within one-phase fields, where no phase transformation was taking place and also of those cases in which so large a difference was imposed between the new and initial temperature that the transformation was from one single-phased state all the way to another single-phased state. The insert sketch, included in this and subsequent time-resistance plots, indicates the portion of the equilibrium resistance-temperature curve within which the equilibrium state is being changed.



Schematic representation of a typical time resistance plot, temperature constant.

FIGURE 7



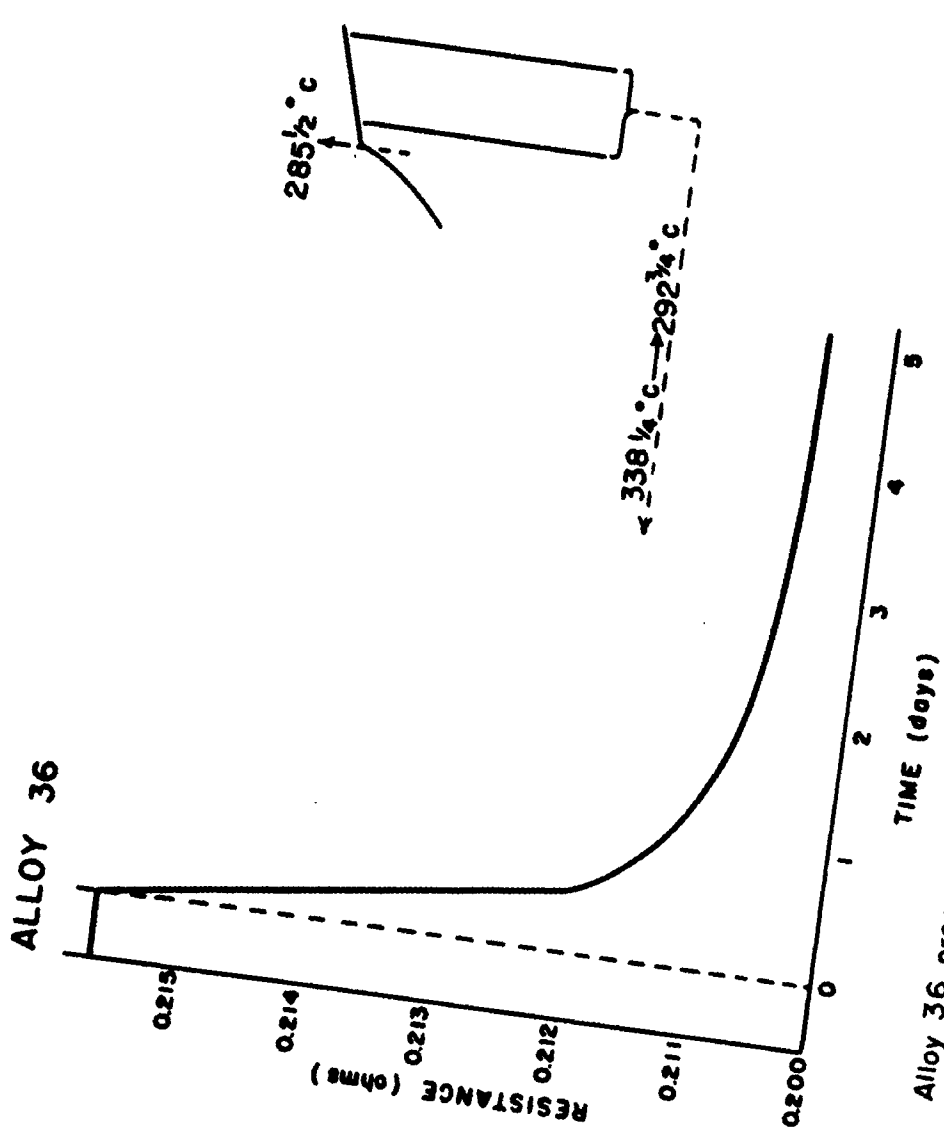
Alloy 25 progressing from equilibrium of 410°C to equilibrium at 395°C.

FIGURE 8

With temperature change wholly within the region of the disordered phase (high temperature), equilibrium was usually attained within a matter of minutes. The crystallographic change involved is merely one of adjustment of the degree of short range order and is expected to be rapid, because diffusion over very short distance is the only time consuming process involved. The very pronounced effect of the slowing of diffusion at lower temperatures was apparent, however, in the alloys near 36 atomic percentage gold, Figure 9, which remain disordered at relatively low temperatures; the time for the attainment of disordered equilibrium increases to a matter of 2 or 3 days just above the transformation temperature. The latter effect was evident also in the approach to equilibrium within the region of the ordered phase, Figure 10. Below about 200°C progress was so slow that it is doubtful that equilibrium was ever attained.

Where a change of phase was involved, as in the transformation from disordered to ordered CuAu, there was always an induction period, Figure 11, but its duration generally decreased with an increasing magnitude of temperature change, i. e., with the degree of undercooling. This is characteristic of a process which involves the nucleation of a new phase. The rate of nucleation increases, at first, with the extent of undercooling. Since this kind of transformation is essentially diffusionless, the growth rate is high and the transformation proceeds very rapidly once nuclei are present. Rather unexpectedly it was found that the induction period was much longer when, instead of lowering, the temperature was raised, so as to cause the alloy to change in one step from an ordered to a disordered state, Figure 12. A possible explanation of this difference is that a larger nucleus is required to establish the disordered than the ordered state, requiring a longer time for the appearance of disordered clusters of suitable size.

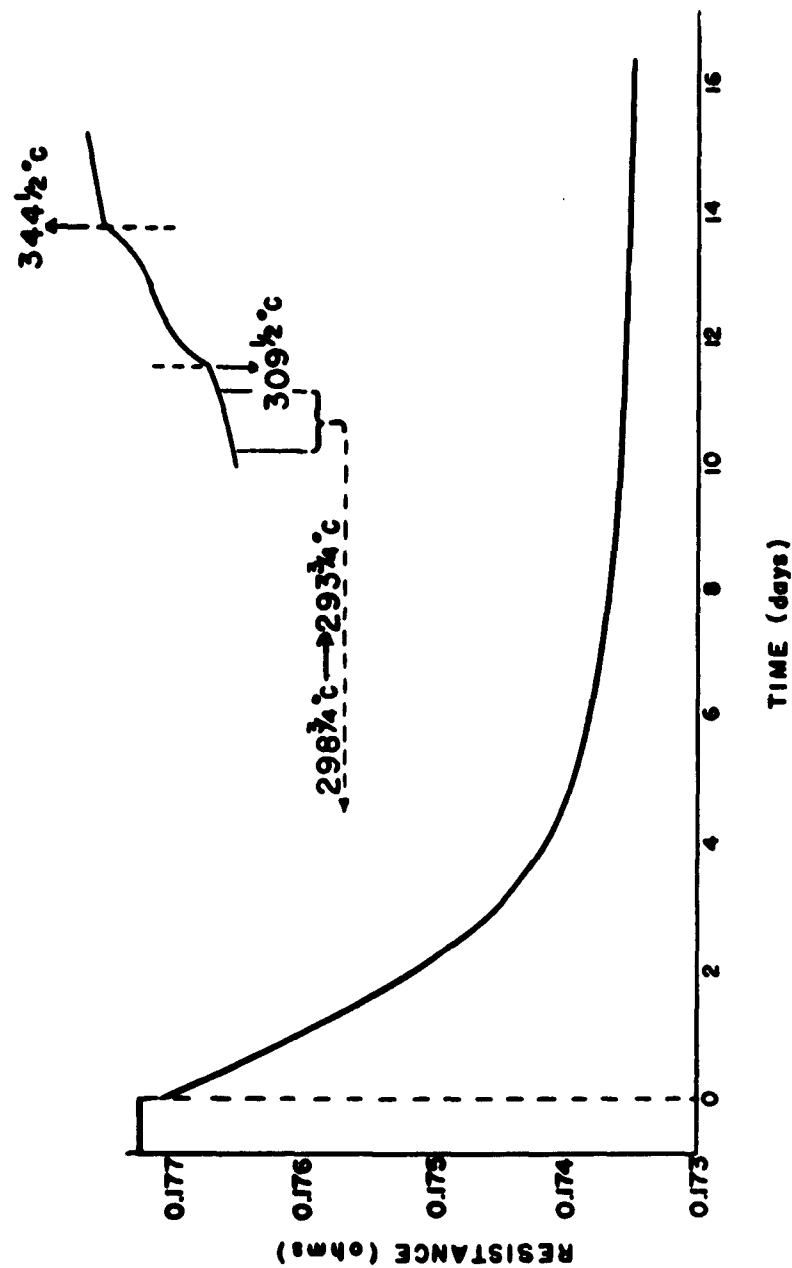
A large increase in the total time required to attain equilibrium was immediately noticeable when a small temperature change, calling for transformation from a one-phase to a two-phase state, or from one two-phase state to another, was imposed, Figure 13.



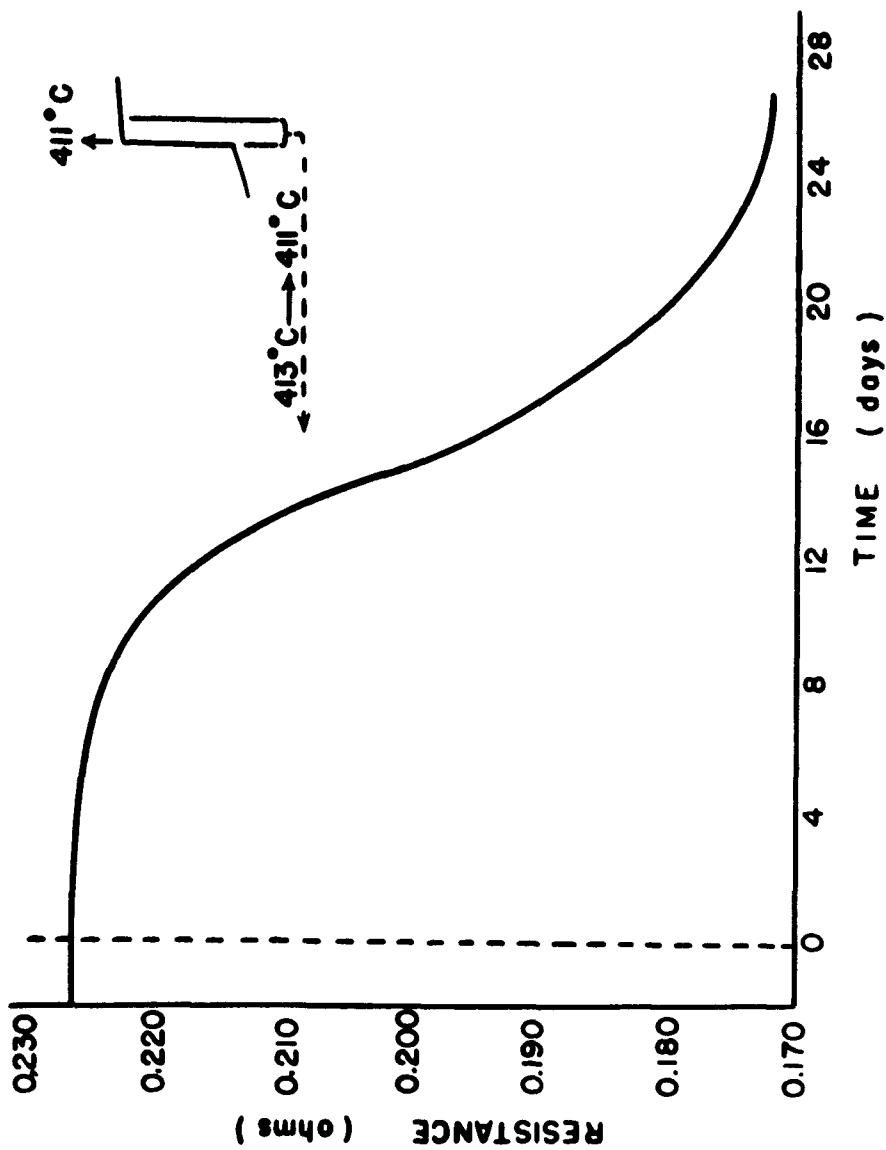
Alloy 36 progressing from equilibrium at 338¼°C to equilibrium at 292¼°C.

FIGURE 9

ALLOY 32

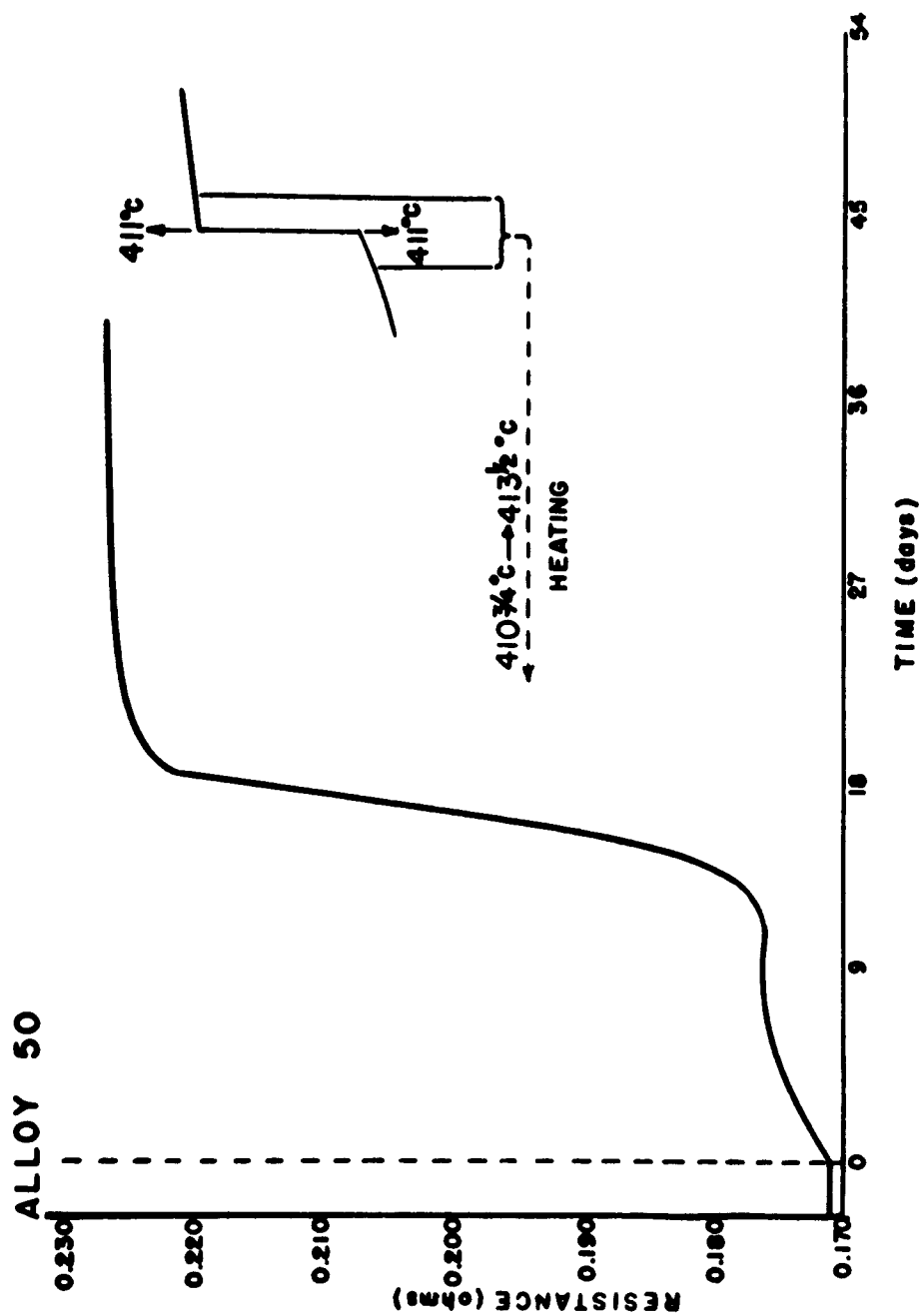


Alloy 32 progressing from equilibrium at 298 3/4 °C to equilibrium at 293 3/4 °C.
FIGURE 10



Alloy 50 progressing from equilibrium at 413°C to equilibrium at 411°C.

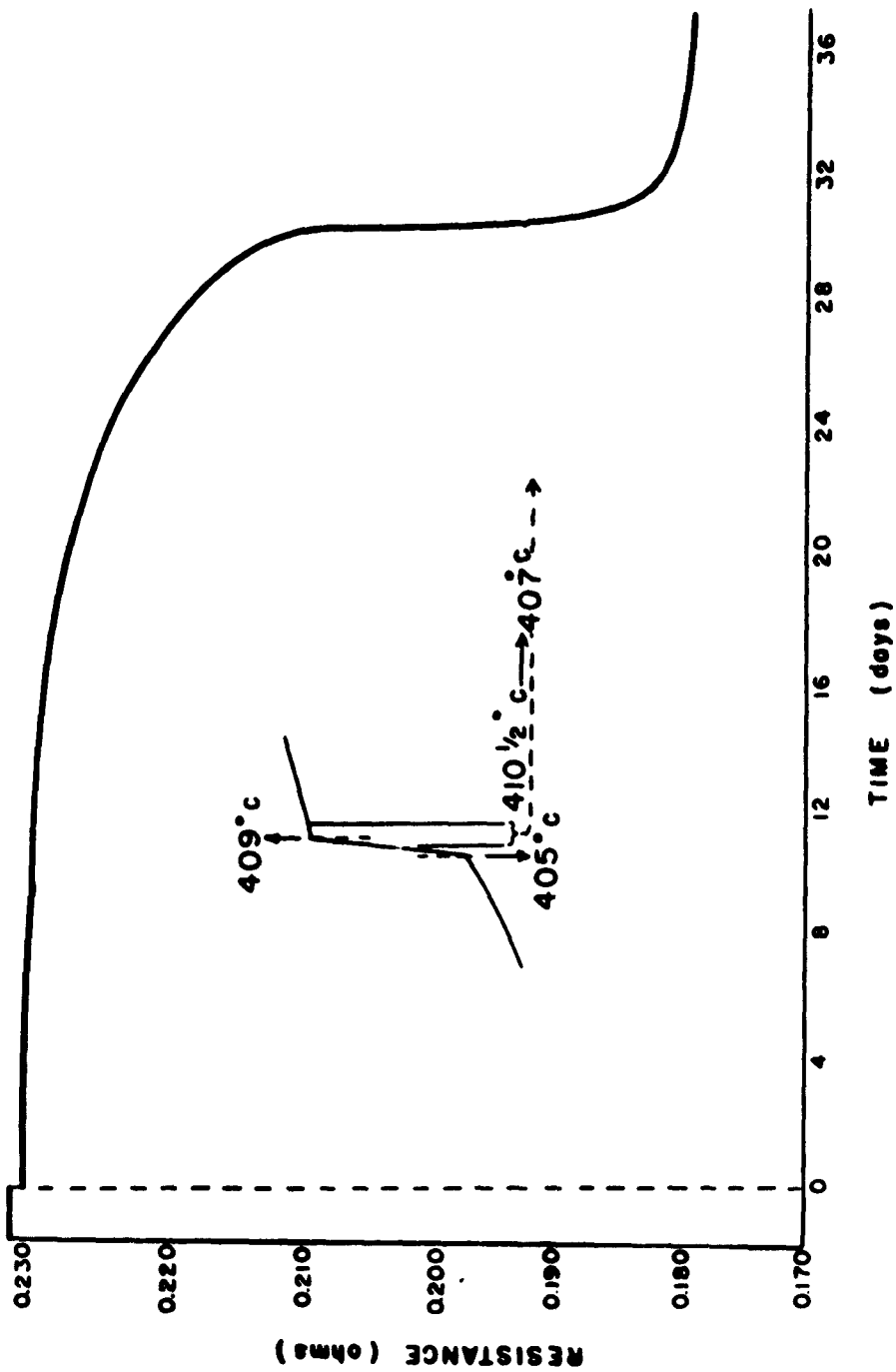
FIGURE 11



Alloy 50 progressing from equilibrium at 410 $\frac{3}{4}$ °C to equilibrium at 413 $\frac{1}{2}$ °C.

FIGURE 12

ALLOY 47



Alloy 47 progressing from equilibrium at 410 1/2°C to equilibrium at 407°C.

FIGURE 13

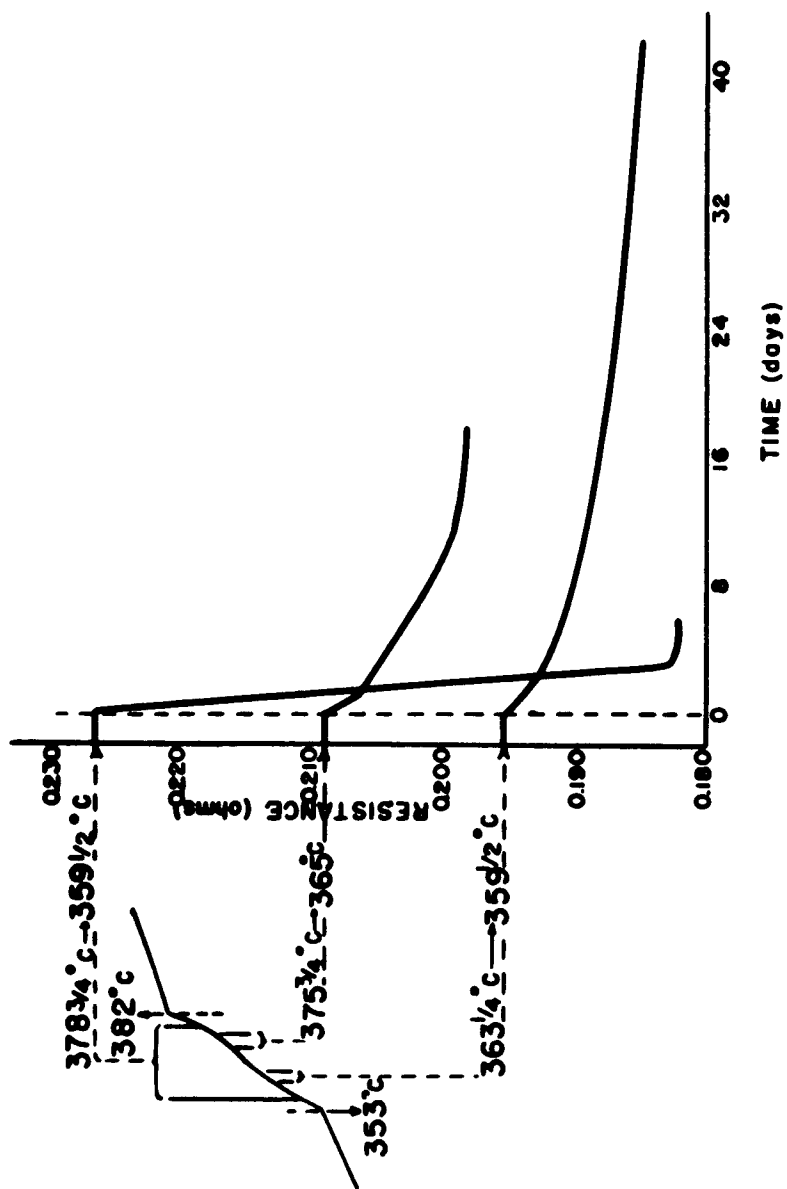
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In the former of these two cases, both the induction period and the subsequent period of resistance change are magnified. This is also to be expected, because the composition of the nucleus must differ from the gross composition of the alloy and the growth of particles of the new phase can proceed only so fast as material of the proper composition is delivered by diffusion from considerable distance. The case for the change from one two-phase equilibrium to another, a few degrees above or below, differs only in that there is no nucleation requirement, and accordingly no induction period, since particles of both phases are already present. Here it is noteworthy, however, that the approach to equilibrium (the growth of particles of the waxing phase) is the more rapid the larger the temperature change, Figure 14, presumably because of the larger composition potential and the correspondingly larger diffusion velocity thus imposed.

It is interesting to observe also, that for a given temperature change, the rate of transformation from a one-phase state to a two-phase state is smaller near the stoichiometric compositions of CuAu and Cu_3Au than it is away from these compositions, Figure 15. Perhaps this is because the ordus and disordus boundaries are nearly horizontal in this region, making the tie-lines longer and calling for a larger chemical segregation between the two phases that are required to coexist, i.e., more diffusion.

The greater reluctance to transform in the direction of disordering is also very marked in one-phase to two-phase transformations. An impressive example of this was encountered in the 32 atomic percentage gold alloy, which, after ordering at a sub-critical temperature, was superheated 10°C above the ordus line and held three months without the development of any of the disordered phase. Upon subsequent heating to 20°C above the ordus, the disordering transformation began and then continued, even when the temperature was dropped back to a few degrees above the ordus. This is clearly an example of an extremely slow nucleation rate for the disordered phase.

ALLOY 43



Alloy 43 progressing from equilibria respectively at $378\frac{3}{4}^{\circ}\text{C}$, $375\frac{3}{4}^{\circ}\text{C}$, and $363\frac{1}{4}^{\circ}\text{C}$ to equilibria at $359\frac{1}{2}^{\circ}\text{C}$, 365°C , and $359\frac{1}{2}^{\circ}\text{C}$.

FIGURE 14

The influence of departure from stoichiometric composition upon the rates of approach to equilibrium is made somewhat ambiguous by the fact that the temperatures of two-phase coexistence decrease simultaneously. Thus, the slower transformation rates, near the minimum in the disorder and at the extremes of the composition range studied, may be due solely to the slower diffusion rates at low temperatures. So great is the difference in rate, however, especially in the middle region, near 36 atomic percentage gold, that it seems probable that the lower degree of perfection of the non-stoichiometric ordered state contributes to the slackening of the rate of phase change, by decreasing the energy difference between the ordered and disordered states.

VII STUDIES UPON THE SYSTEM COBALT-PLATINUM

Attempts to conduct similar studies upon ordering alloys of the system cobalt-platinum were complicated by a number of factors, among the least of which was the higher transformation temperature and the equipment modification so dictated. Most troublesome was the finding that in the range about CoPt there is almost no difference between the electrical resistivity of the disordered phase and that of the ordered phase. This is shown by an equilibrium trace through the temperature range of ordering in the 46 atomic percentage platinum alloy, Figure 16. Studies conducted at the General Electric Company Research Laboratories had indicated that the same alloys, if quenched from stabilization at the higher temperatures, exhibit, at room temperature a significant difference in the resistivity of the two states.

An effort was made, therefore, to establish the resistance-temperature curve by withdrawing the specimen assemblies from the furnace, after equilibrium had presumably been attained and quenching them in ice water before making the resistance measurements. Curves of the type of that of Figure 17 were thus produced. It will be noted, however, that there is wide scatter in the datum points, particularly as between measurements made upon descending and ascending cycles of temperature change. This scatter may result from a failure to establish true equilibrium before quenching, or it may be due to uncontrolled differences in the manner of quenching. Whatever the cause, it was felt that the present experimental method is not well adapted to the study of the cobalt-platinum alloys and that the construction of a phase diagram upon the basis of the data obtained is not warranted.

These observations do show, however, that resistance-temperature curves having two inflections (type "b") occur across much of the range of ordering in the cobalt-platinum system. It may be inferred therefrom that this transformation also proceeds as a normal phase change and, at least in this respect, is similar to the transformations in the copper-gold system.

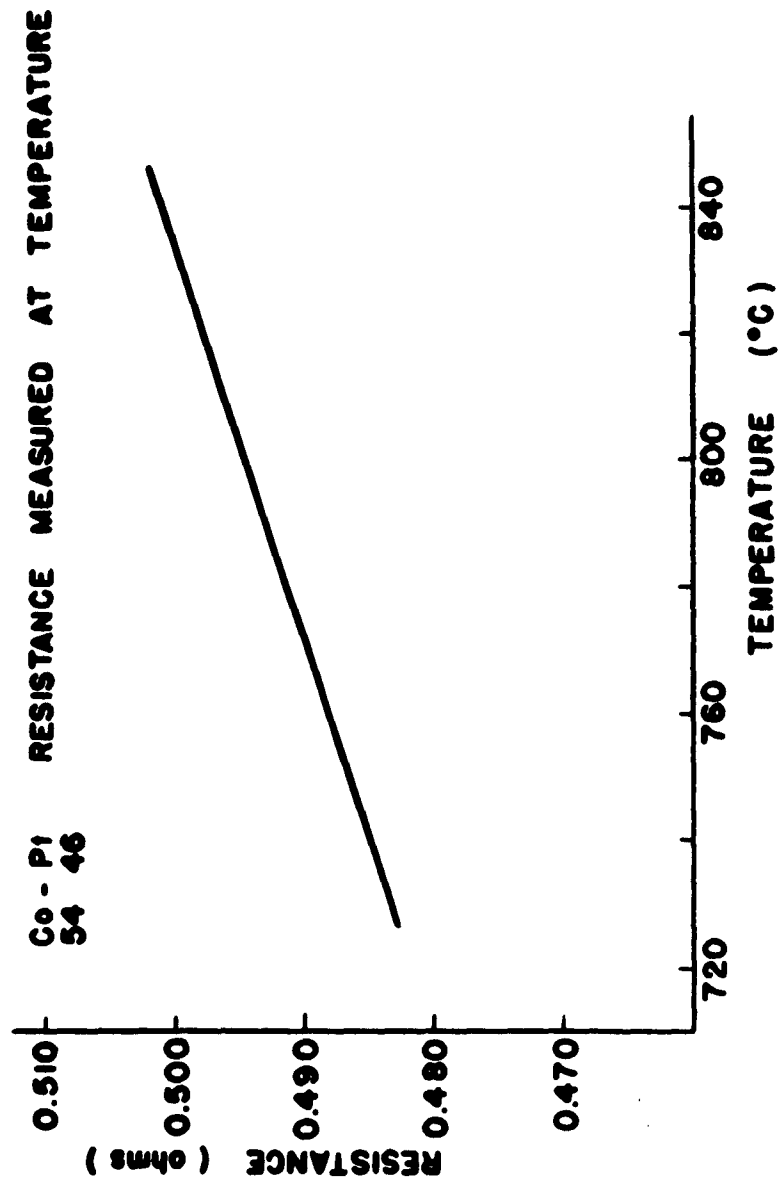
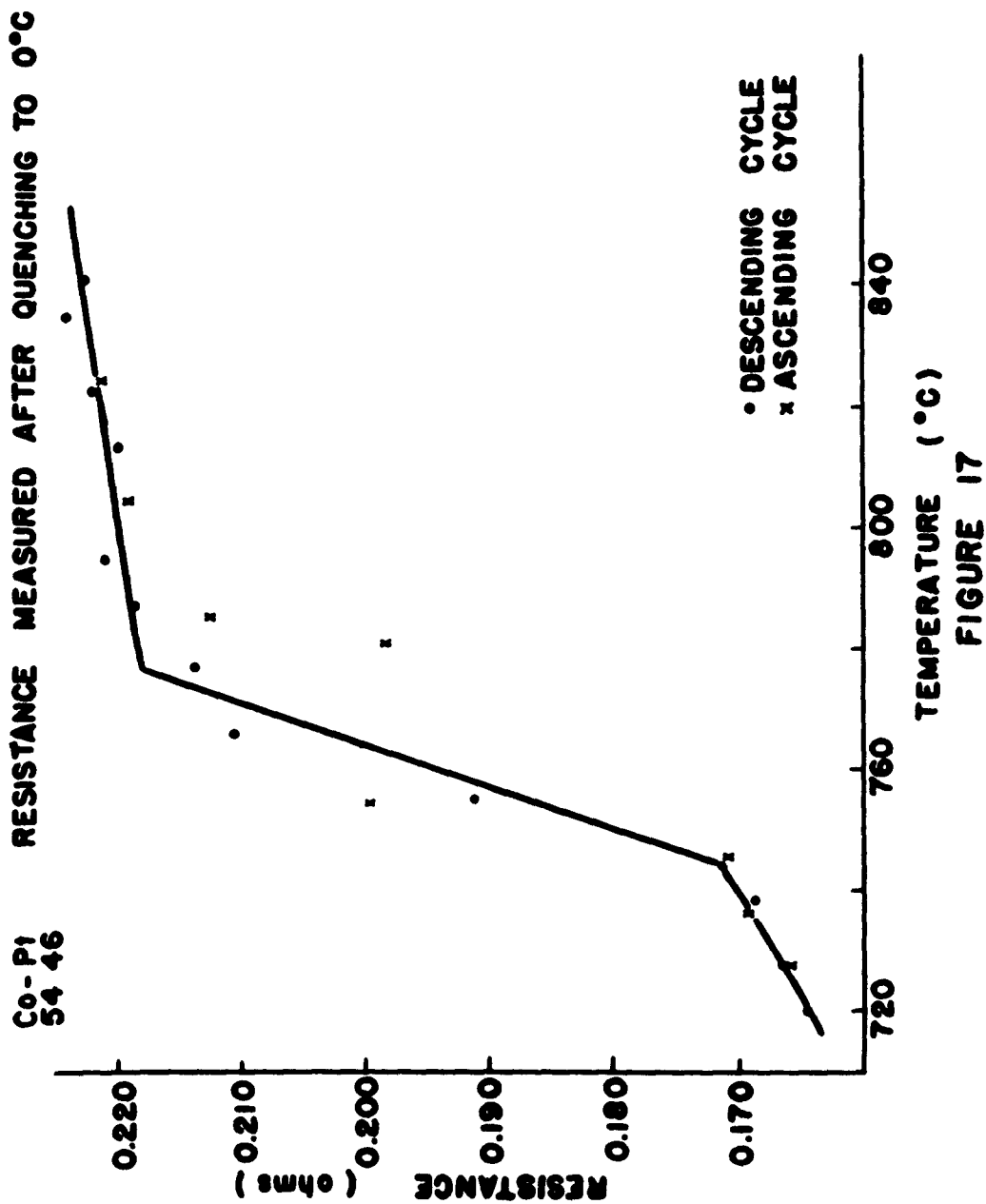


FIGURE 16



VIII DISCUSSION

The observations that have been described make it clear that the copper-gold phase diagram of Haughton and Payne is correct in its general form, except for the inclusion of a fourth solid phase near 41 atomic percentage gold. Neither the present equilibrium studies, nor X-ray diffraction studies, provide any basis for postulating the existence of this phase. The diagram presented in Figure 5 is believed to be more precise than the Haughton and Payne diagram, especially in the location of the ordus boundaries, the positions of which were only crudely estimated in the earlier work. Good agreement exists between the short span of disorder recently determined by Newkirk⁵, using X-ray diffraction measurements and the corresponding section of the boundary in Figure 5. Less perfect agreement exists with Newkirk's corresponding section of ordus curve, which lies in a composition range several percent higher in gold content than that section of the curve established by the present studies.

That a eutectoid reaction exists near 36 atomic percentage gold and 284°C, seems almost inevitable. A degree of uncertainty must be recognized, however, in the failure of the equilibrium measurements to report an isothermal resistivity change at this temperature. An adequate reason for this behavior is to be found in the extreme sluggishness of reaction in this composition range, but the fact remains that the existence of the eutectoid can be argued only from the observation that three two-phase regions meet at this location. It is perhaps worthy of note that the CuAu + Cu₃Au region that exists below the eutectoid has a span of nearly 5 atomic percentage gold. Preston,⁶ in 1931, was unable to detect the co-existence of these two phases and concluded that the two-phase region must be very narrow indeed.

Of particular interest is the observation that the low temperature phase near 70 atomic percentage gold exhibits higher resistivity than the high temperature phase, at the same temperature. This has not been predicted, and no explanation can be offered here. So little is presently known of the characteristics of CuAu₃ that it remains difficult to associate the observations presently in hand.

The rate studies leave little room for doubt that the ordering and disordering reactions proceed as conventional nucleation and growth processes. The nucleation rate, estimated from the inverse of the induction period, increases with undercooling and superheating, as it should. It also increases as the composition difference between the precipitating and parent phases decreases and ceases to be significant where no new phase is appearing. The growth rate is obviously responsive to the requirements of diffusion, being very high, as should be expected, where no composition change is requisite to growth and low where the precipitating phase differs in composition from the parent phase.

Although others have proposed that the ordering reaction occurs as a nucleation and growth process, this clear demonstration is important, because it shows that the homogeneous transformation concept, upon which the modern order-disorder transformation theory has been constructed, is untenable. Some comfort is to be derived, however, from the fact that a nucleation and growth process, framed within the limitations of phase equilibria, leads qualitatively, at least, to the same predictions with respect to the forms of electrical resistivity and specific heat curves, as does the modern theory.

IX CONCLUSIONS

1. By means of measurements made at equilibrium, the order and disorder boundaries of the system copper-gold have been accurately located and the existence of such conjugate boundaries has been proved; a new phase diagram is presented.
2. A eutectoid transformation (disorder to ordered CuAu and ordered Cu₃Au) occurs at about 36 atomic percentage gold and 284°C.
3. The existence of a field of coexistence of the ordered phases Cu₃Au and CuAu, between about 35 and 40 atomic percentage gold, has been demonstrated.
4. There is no evidence of an intermediate phase at 41 atomic percentage gold, such as had been postulated by Haughton and Payne.
5. Evidence exists of the occurrence of another phase near 70 atomic percentage gold; this phase has higher electrical resistivity than the conjugate disordered phase at like temperature.
6. A copper-gold alloy, containing 66 atomic percentage gold, exhibits a nearly zero temperature coefficient of electrical resistivity between 240° and 270°C and a very small coefficient at higher temperature.
7. Ordering in the copper-gold system proceeds in a manner typical of phase changes that occur by nucleation and growth processes.
8. Incomplete studies indicate that two-phase (order plus disorder) regions exist in the system cobalt-platinum in a manner analogous to their occurrence in the copper-gold system.

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